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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C09J 4/06, C08F 287/00	A1	(11) International Publication Number: WO 93/20164 (43) International Publication Date: 14 October 1993 (14.10.93)
(21) International Application Number: PCT/US93/02528 (22) International Filing Date: 19 March 1993 (19.03.93) (30) Priority data: 07/861,242 31 March 1992 (31.03.92) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: ALI, Mahfuza, B. ; BABU, Gaddam, N. ; ZIMMERMAN, Patrick, G. ; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).		(74) Agents: DOWDALL, Janice, L. et al. ; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (81) Designated States: JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ULTRAVIOLET RADIATION CURABLE ACRYLATE PRESSURE-SENSITIVE ADHESIVE COMPOSITIONS (57) Abstract Crosslinked networks of (meth)acrylate (co)polymers, and a method of making the networks, are provided in which a photoiniferter-derived homopolymer, random copolymer or block copolymer is dissolved in a compatible monomer mixture along with a radiation-sensitive photoinitiator and crosslinker. The polymer-monomer mixture is coated onto a suitable web and cured via ultraviolet radiation to yield a crosslinked network resulting from polymerization of monomers along with incorporation of the active photoiniferter polymer. The networks exhibit excellent adhesive properties. When the photoiniferter polymer is a homopolymer, a random copolymer or an AB-type diblock copolymer, a pressure-sensitive adhesive results. When the photoiniferter polymer is a homopolymer or a random copolymer, the resulting adhesive exhibits excellent vibration-damping characteristics. When the photoiniferter polymer is an ABA-type triblock copolymer, a structural adhesive is obtained.		

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**ULTRAVIOLET RADIATION CURABLE ACRYLATE
PRESSURE-SENSITIVE ADHESIVE COMPOSITIONS**

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Field of the Invention

The present invention relates to controllably curable adhesive compositions which depending upon the particular formulation can upon cure provide polymers exhibiting pressure-sensitive adhesive properties, and optionally vibration damping properties, and optionally structural adhesive properties.

Background of the Invention

Acrylate pressure-sensitive adhesives are well known in the art. Ulrich (U.S. Reissue No. 24,906) describes alkyl acrylate copolymers comprising a predominant amount of C₄- to C₁₄-alkyl esters of acrylic acid and a minor amount of a copolymerizable polar monomer such as acrylic acid. Such adhesives are widely popular due to their availability, low cost, and ability to provide the requisite fourfold balance of adhesion, cohesion, stretchiness, and elasticity known to be required for an effective pressure-sensitive adhesive.

Subsequent references suggest various modifications in the basic acrylic polymer to enhance various physical properties in the PSA composition. For example, Martens et al. (U.S. Patent No. 4,181,752) discloses the exposure of an acrylic polymer to ultraviolet radiation to achieve crosslinking and enhance shear strength. Harlan (U.S. Patent No. 3,239,478) discloses the preparation of block or segmented copolymers to provide PSA compositions which have improved strength and overall PSA properties because of phase separation of soft butadiene or butadiene-isoprene polymer blocks and hard polystyrene blocks of the block copolymer.

Another well-known method of modifying acrylic pressure-sensitive adhesives is to form a syrup comprising a pre-formed acrylic polymer or oligomer and an acrylic monomer. The pre-formed polymer can be inert or reactive under subsequent polymerization or crosslinking reactions. Japanese Patent No. 56-161,484 describes the thermal free-radical polymerization of a vinyl monomer in the presence of an acrylic polymer to produce an acrylic pressure-sensitive hot-melt adhesive. Glennon (U.S. Patent No. 4,243,500) describes an adhesive produced by dissolving an elastomer in an acrylate ester monomer wherein a significant amount of added tackifier is

required to obtain satisfactory adhesion levels. Canadian Patent No. 1,192,688 discloses an adhesive composition comprising a high glass transition temperature (T_g) acrylic monomer in which is dispersed a core-shell polymer, to produce a 100% reactive fluid adhesive on subsequent curing of the monomer.

Addition of polymers which cannot react with acrylate monomers, followed by polymerization of the monomers usually results in macrophase phase separation due to the lack of interconnectivity of the resulting two polymer systems.

Photoiniferter technology is a recently developed technology which allows for the polymerization of block copolymers from various monomers. The control of the polymerization provided by the photoiniferter technology permits "tailoring" of the block copolymers formed thereby so that polymers having a wide spectrum of physical properties can be prepared. Such high precision tailoring is not possible with previously known polymerization methods such as thermal polymerization.

The term "photoiniferter" refers to a chemical compound that has a combined function of being a free-radical initiator, transfer agent, and terminator, the term "iniferter" being a word formed by the underlined portions of the terms identifying these functions. The "photo" portion of the term indicates that the polymerization is photolytically induced. This term and its use in the production of block copolymers is well known, particularly because of the work of Takayuki Otsu of the Department of Applied Chemistry, Osaka City University, Osaka, Japan. This work is discussed, for example, in an article by Otsu et. al. entitled "Living Radical Polymerizations in Homogeneous Solution by Using Organic Sulfides as Photoiniferters," Polymer Bulletin, 7, 45-50 (1982), and an article by Otsu et. al. entitled "Living Mono- and Biradical Polymerizations in Homogeneous System Synthesis of AB and ABA Type Block Copolymers," Polymer Bulletin, 11, 135-142 (1984), and in European Patent Application 0,286,376, published October 12, 1988.

Copending U.S. Application Serial No. 07/596,575, filed October 11, 1990, which is a Continuation-in-Part of U.S. Application Serial No. 07/356,650, filed May 19, 1989, which is a Continuation-in-Part of U.S. Application Serial No. 07/212,594, Ali, et al., filed June 28, 1988, and European Patent Application No. 89.306516.9 published January 3, 1990, (all assigned to the assignee of the present case) disclose the use of iniferter

technology in the preparation of acrylic block copolymers having the requisite physical properties of adhesion, cohesion, stretchiness and elasticity, making them suitable for use in pressure-sensitive adhesive compositions.

Copending U.S. Application Serial No. 07/501,273, Ali et al.,
5 filed May 29, 1990 (assigned to the assignee of the present case) provides certain acrylate copolymer adhesives produced by photoiniferter technology which are useful for the assembly of microelectronic devices.

In none of the above cases, however, is there disclosed a
pressure-sensitive adhesive which also possesses vibration-damping and/or
10 structural adhesive characteristics.

European Patent Application 0,286,376, published October 12,
1988, provides ABA-type block copolymers made using photoiniferter
technology, in which the constituent B-block (soft) monomers are acrylic acid
esters and the A-block (hard) monomers are methacrylic esters, maleimido or
15 aromatic vinyl derivatives. The resultant polymers are claimed to be in the form of an elastomer, sealant, packing, adhesive material, vibration-proof material, sound absorbing material, soiling material or hose. These polymers are specifically limited to ABA blocks of the monomers listed above. No added photoinitiator is present, and no post-coating ultraviolet radiation (UV) cure is
20 taught or suggested.

Japanese Patent Application (Kokai) 64-29410, laid open
January 31, 1989, discloses a UV-curable pressure-sensitive adhesive prepared using photoiniferter technology. Typically, a vinyl monomer or vinyl monomer
mixture is photopolymerized in the presence of a dithiocarbamate to make a
25 polymeric photoiniferter. The dithiocarbamate-terminated polymer is then mixed with one or more monomers, at least one of which must be a multifunctional (i.e., two or more vinyl groups) monomer such as HDDA, and a photoinitiator. The mixture is coated and cured with UV light. No attempt was made to optimize the resulting polymer for vibration-damping use, and
30 such use is not taught or suggested. The application gives no indication that there is any interaction between the photoiniferter polymer and the photopolymerized (multi)functional monomer. In other words, all of the PSA properties arise from the photoiniferter polymer and none from the added photopolymerized monomer.

35 The use of acrylate copolymers for vibration-damping purposes is disclosed in U.S. Patent Nos. 4,034,639; 3,605,953; and 3,537,717. The polymers are not produced by photochemical polymerization procedures, and

are not inherently adhesive, so that a separate adhesive must be used to adhere the vibration-damping polymer to a substrate. U.S. Patent No. 3,986,581 discloses an acrylate copolymer produced by conventional photopolymerization processes which possesses vibration-damping properties, but the polymer is not
5 an adhesive, so a separate adhesive is required for application of the polymer to a substrate. European Patent Application 390,207, published October 3, 1990, discloses a pseudo-IPN comprising a vinylidene fluoride/hexafluoropropylene copolymer dissolved in an acrylate monomer which is subsequently polymerized thermally or photochemically, then coated and crosslinked. Crosslinking occurs
10 in the fluoroelastomer or the acrylate or both. No PSA properties are taught or claimed for this fluoroelastomer/acrylate system.

A need thus exists for a pressure-sensitive adhesive composition which can be controllably cured by exposure to ultraviolet radiation and which depending on the formulation can upon cure provide pressure-sensitive adhesive
15 properties, optionally vibration damping properties, and optionally structural adhesive properties. We have found such a pressure-sensitive adhesive composition.

Summary of the Invention

20 The present invention relates to radiation curable acrylate compositions each comprising a single phase blend of photopolymerizable vinyl-group containing monomers, a radiation activatable crosslinking agent, a photoinitiator, and a photoiniferter polymer having one or more reactive end groups, wherein the single phase blends can be coated onto a substrate as a
25 syrup and subsequently subjected to sufficient radiant energy to effect crosslinking. The crosslinked polymer systems thus obtained possess excellent properties for use as pressure-sensitive adhesives, optionally vibration-dampers, and optionally structural adhesives.

The present invention relates to a radiation curable pressure-sensitive adhesive composition comprising:

- 30 (a) 100 parts by weight of free radically (co)polymerizable monomer comprising:
- (i) about 80 to about 100 parts by weight of (meth)acrylic acid ester(s) of monohydric alcohol(s), wherein said monohydric
35 alcohol(s) comprise an average of about 1 to about 12 carbon atoms; and

(ii) about 0 to about 20 parts by weight of monoethylenically unsaturated polar monomer(s) which are copolymerizable with the (meth)acrylic acid ester(s);

(b) about 10 to about 100 parts by weight of a photoiniferter polymer selected from the group consisting of $I(BT)_n$ wherein n is an integer of 1 to 2, $I(BAT)_n$ wherein n is an integer of 1, and mixtures thereof, wherein

B comprises a polymer block having a T_g of between about -70°C and about 0°C wherein the polymer block B comprises polymerizable monoethylenically-unsaturated monomer(s);

A comprises a polymer block having a T_g of between about $+30^\circ\text{C}$ and about $+160^\circ\text{C}$ wherein the polymer block A comprises polymerizable monoethylenically-unsaturated monomer(s);

I represents a free-radical initiator portion of an iniferter of the formula $I(T)_n$, wherein

T represents the terminator portion of said iniferter; and

$I(T)_n$ is capable upon being subjected to an appropriate energy source of forming free radicals $I(\cdot)_n$ and $nT\cdot$ wherein $I\cdot$ is a highly reactive free radical capable of initiating free radical polymerization, and $T\cdot$ is a less reactive free radical which is generally much less capable of initiating free radical polymerization than $I\cdot$ but will rejoin with $I(\cdot)_n$ upon termination of said energy source;

(c) about 0.1 to about 5 parts by weight of a radiation-activatable crosslinking agent based upon the total weight of (a) plus (b); and

(d) about 0.01 to about 5 parts by weight of a photoinitiator based upon the weight of (a).

The present invention also relates to a vibration damping composition comprising:

(a) 100 parts by weight of free-radically (co)polymerizable monomer comprising:

(i) about 80 to about 100 parts by weight of (meth)acrylic acid ester(s) of monohydric alcohol(s), wherein the monohydric alcohol(s) comprise an average of about 1 to about 12 carbon atoms;

(ii) about 0 to about 20 parts by weight of monoethylenically unsaturated polar monomer(s) that are copolymerizable with the (meth)acrylic acid ester(s);

-6-

(b) about 10 to about 100 parts by weight of a photoiniferter polymer selected from the group consisting of $I(BT)_n$, and mixtures thereof, wherein

n is an integer of 1 to 2;

5 B comprises a polymer block having a T_g of between about -70°C and about -15°C , and a number average molecular weight ranging from about 20,000 to about 50,000, wherein polymer block B comprises polymerizable monoethylenically-unsaturated monomer(s);

10 I represents a free-radical initiator portion of an iniferter of the formula $I(T)_n$, wherein

T represents the terminator portion of the iniferter; and

$I(T)_n$ is capable upon being subjected to an appropriate energy source of forming free radicals $I(\cdot)_n$ and $nT\cdot$ wherein $I\cdot$ is a highly reactive free radical capable of initiating free radical polymerization, and $T\cdot$ is
15 a less reactive free radical which is generally much less capable of initiating free radical polymerization than $I\cdot$ but will rejoin with $I(\cdot)_n$ upon termination of the energy source;

(c) about 0.1 to about 5 parts by weight of a radiation-activatable crosslinking agent based upon the total weight of (a) plus
20 (b); and

(d) about 0.01 to about 5 parts by weight of a photoinitiator based upon the weight of (a).

The present invention also relates to a structural pressure-sensitive adhesive composition comprising:

25 (a) 100 parts by weight of free radically (co)polymerizable monomer comprising:

(i) about 80 to about 100 parts by weight of (meth)acrylic acid ester(s) of monohydric alcohol(s), wherein the monohydric alcohol(s) comprise an average of about 1 to about 12 carbon atoms; and

30 (ii) about 0 to about 20 parts by weight of monoethylenically unsaturated polar monomer(s) that are copolymerizable with the (meth)acrylic acid ester(s);

(b) about 10 to about 100 parts by weight of a photoiniferter polymer selected from the group consisting of $I(BAT)_n$, and mixtures thereof
35 wherein

n is an integer of 2;

B comprises a polymer block having a T_g of between about 0°C and about -70°C, wherein polymer block B comprises polymerizable monoethylenically-unsaturated monomer(s);

5 A comprises a polymer block having a T_g of about 30°C to about 160°C wherein polymer block A comprises polymerizable monoethylenically-unsaturated monomer(s);

I represents a free-radical initiator portion of an iniferter of the formula $I(T)_n$, wherein

10 T represents the terminator portion of said iniferter; and $I(T)_n$ is capable upon being subjected to an appropriate energy source of forming free radicals $I(\cdot)_n$ and $nT\cdot$ wherein $I\cdot$ is a highly reactive free radical capable of initiating free radical polymerization, and $T\cdot$ is a less reactive free radical which is generally much less capable of initiating free radical polymerization than $I\cdot$ but will rejoin with $I(\cdot)_n$ upon termination
15 of said energy source;

(c) about 0.1 to about 5 parts by weight of a radiation-activatable crosslinking agent based upon the total weight of (a) plus (b); and

20 (d) about 0.01 to about 5 parts by weight of a photoinitiator based upon the weight of (a).

An advantage of the compositions of the invention is the unique morphology and excellent balance of properties of the crosslinked polymer systems prepared therefrom and the minimization of phase separation due to incorporation of the photoiniferter polymer through its reactive end group(s).

25 Another advantage of the compositions of the invention is that the photoiniferter technology employed allows precise tailoring of the resultant crosslinked polymer system to maximize the effectiveness of the resultant material.

30 Detailed Description of the Invention

I. Photoiniferter Polymer

The compositions of the invention may comprise photoiniferter polymer selected from the group consisting of $I(BT)_n$, $I(BAT)_n$, and mixtures
35 thereof, depending upon the particular composition.

Photoiniferter polymer $I(BT)_n$ is made by reaction of a photoiniferter and an acrylic monomer. The terms "photoiniferter" and "iniferter" are used interchangeably herein. An iniferter, represented by the general formula $I(T)_n$, is capable, upon being subjected to an appropriate energy source, of forming free radicals $I(\cdot)_n$ and $nT\cdot$ wherein n is an integer of 1 to 2, $I\cdot$ is a highly reactive free radical capable of initiating free-radical polymerization, and $T\cdot$ is a less-reactive free-radical which is generally much less capable of initiating free-radical polymerization than $I\cdot$ but will rejoin with $I(\cdot)_n$ or a free-radical polymer segment which is free-radically polymerized with $I(\cdot)_n$ upon termination of the energy source. Such an iniferter is mixed with a first monomer charge comprising acrylic monomer(s) which are free-radically polymerizable in the presence of $I(\cdot)_n$ to form an acrylic polymer block which may be a homopolymer or a random copolymer. The mixture is exposed to an energy source capable of forming free radicals $I(\cdot)_n$ and $nT\cdot$ arising from the iniferter. The exposure is maintained until the first monomer charge polymerizes with $I(\cdot)_n$ to form a free-radical polymer segment represented by the formula $I(B\cdot)_n$, wherein B represents a homopolymer or random copolymer block. When the exposure is terminated, $I(B\cdot)_n$ and $nT\cdot$ combine to form a polymer represented by the formula $I(BT)_n$. It is theorized that iniferters wherein n is an integer of 3 or 4 would also be useful according to the invention.

In order to prepare a photoiniferter block copolymer of the formula $I(BAT)_n$, $I(BT)_n$ is mixed with a second monomer charge comprising monomer(s) which are free-radically polymerizable in the presence of $I(B\cdot)_n$ to form a thermoplastic reinforcing polymer block A. The monomer(s) from which block A is formed thus are not the exact same monomer(s) from which block B is formed. $I(BT)_n$ is exposed to an energy source capable of producing free radicals $I(B\cdot)_n$ and $nT\cdot$. The exposure is maintained until the second monomer charge polymerizes with $I(B\cdot)_n$ to form a free-radical block copolymer segment represented by the formula $I(BA\cdot)_n$ wherein A represents a relatively hard polymer block formed of the second monomer charge. When exposure is terminated, $I(BA\cdot)_n$ and $nT\cdot$ combine to form a block copolymer represented by the formula $I(BAT)_n$.

In the case of block copolymers wherein two monomer charges are used, when n is 1 the polymer which results is an AB-type block copolymer; when n is 2, an ABA-type block copolymer results.

The photoiniferter polymer typically has a number average molecular weight in the range of about 15,000 to about 500,000 depending upon the intended application of the final cured polymer system, as will be explained below in more detail. Preferably, the compositions of the invention
5 comprise about 20 to about 30 parts by weight photoiniferter polymer in order to provide superior adhesive properties.

Polymer Block B

As indicated above, the polymer block B of the $I(BT)_n$ or
10 $I(BAT)_n$ photoiniferter polymer can comprise a homopolymer or a random copolymer of two or more free-radically (co)polymerizable monomers. Examples of monomers which polymer block B can comprise include but are not limited to those selected from the group consisting of nonpolar vinyl monomers such as styrene, t-butyl styrene, methyl methacrylate, ethyl
15 methacrylate, n-butyl methacrylate, methyl acrylate, butyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, isobornyl acrylate, and mixtures thereof. The term "nonpolar" monomer as defined herein includes both nonpolar and moderately polar monomers. Preferred nonpolar monomers include those selected from the group consisting of butyl acrylate, isooctyl acrylate,
20 2-ethylhexyl acrylate, and mixtures thereof, for reasons of performance, availability and cost.

Another type of monomer which the polymer block B can comprise is a polar monoethylenically-unsaturated monomer that is copolymerizable with the aforementioned nonpolar monomers. Examples of
25 useful polar monomers include but are not limited to those selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, acrylonitrile, methacrylonitrile, N-vinylpyrrolidone, polyethylene oxide acrylate, and mixtures thereof. Examples of the polar groups which the monomers may contain include but are not limited to those selected from the
30 group consisting of carboxylic acid, amine, hydroxy, nitrile, and amide groups. The preferred polar monomers are acrylic acid and methacrylic acid, for reasons of enhanced intermolecular interactions of the resulting polymer.

The most preferred embodiment of polymer block B is a random copolymer comprising a nonpolar monomer selected from the group consisting
35 of butyl acrylate, isooctyl acrylate, 2-ethylhexyl acrylate, and mixtures thereof, and a polar monomer selected from the group consisting of acrylic acid, N-vinylpyrrolidone, methacrylic acid, and mixtures thereof.

As indicated above, the photoiniferter polymer can also comprise an AB-type diblock copolymer or an ABA-type triblock copolymer. In these cases, the B-block, as described above, comprises a softer, elastomeric block having a glass transition temperature below about 0°C, as will be noted in further detail below.

Polymer Block A

The A-block of the AB or ABA block copolymers preferably comprises a homopolymer or copolymer formed from free-radically (co)polymerizable monomers selected from the group consisting of methyl methacrylate, poly(styrylethyl) methacrylate, acrylonitrile, isobornyl acrylate, isobornyl methacrylate, N-vinylpyrrolidone, glycidyl methacrylate, and mixtures thereof. These monomers are generally considered to provide "hard" thermoplastic polymers having glass transition temperatures above about 30°C. Most preferably the A-block is prepared from monomers selected from the group consisting of methyl methacrylate, isobornyl methacrylate, isobornyl acrylate, and mixtures thereof, for reasons of performance and availability.

Photoiniferters

Photoiniferters useful for producing the I(BT)_n and I(BAT)_n polymers according to the present invention include but are not limited to those photoiniferters selected from the group consisting of dithiocarbamates, disulfides, and mixtures thereof. Examples of specific useful iniferters include but are not limited to those selected from the group consisting of n-butyl-N,N-dimethyldithiocarbamate; benzyl N-methyldithiocarbamate; benzyl N,N-dimethyldithiocarbamate; benzyl N-ethyldithiocarbamate; benzyl N,N-diethyldithiocarbamate; p-xylylene bis(dithiocarbamate); p-xylylene bis(N-methyldithiocarbamate); p-xylylene bis(N,N-dimethyldithiocarbamate); p-xylylene bis(N-ethyldithiocarbamate); p-xylylene bis(N,N-diethyldithiocarbamate); 1,2-bis(N,N-dimethyldithiocarbamoyl)ethane; 1,2,3-tris(N,N-dimethyldithiocarbamoyl)propane; 1,2,4,5-tetrakis(N,N-diethyldithiocarbamoyl methyl)benzene; thiuram monosulfide; N,N'-dimethylthiuram monosulfide; N,N,N',N'-tetramethylthiuram monosulfide; N,N'-diethylthiuram monosulfide; N,N,N',N'-tetraethylthiuram monosulfide; diphenyl disulfide; thiuram disulfide; N,N'-dimethylthiuram disulfide; N,N,N',N'-tetramethylthiuram disulfide;

N,N'-diethylthiuram disulfide; N,N,N',N'-tetraethylthiuram disulfide; 2-phenylethyl N,N-diethyldithiocarbamate; benzyl carbazoyl dithiocarbamate; xylylene bis(carbazoyl dithiocarbamate); and mixtures thereof. Preferred photoiniferters comprise dithiocarbamates. The most preferred photoiniferters are those selected from the group consisting of benzyl N,N-diethyldithiocarbamate, p-xylylene bis(N,N-diethyldithiocarbamate), and mixtures thereof. The photoiniferter concentration is chosen so as to optimize the molecular weight of the photoiniferter polymer (i.e., the higher the concentration of photoiniferter, the lower the molecular weight of the photoiniferter polymer).

Method of Preparing Photoiniferter Polymer

The polymerization of the monomer(s) to produce the polymer block of the photoiniferter polymer is by step-wise free radical polymerization. The monomer is dissolved in a suitable inert solvent, if needed, and polymerized by a first free radical polymerization utilizing a suitable iniferter as a free radical initiator source. Generally, from about 0.01 to about 5 percent by weight of iniferter based upon the total weight of polymerizable composition (i.e., the total weight of monomers) is used.

The iniferter is caused to dissociate to form free radicals by exposure to an appropriate energy source. The preferred iniferter is one which will dissociate upon exposure to a radiant energy source, most preferably an ultraviolet radiant energy source. Upon exposure to the energy source, the iniferter dissociates to form free radicals which promote free radical polymerization. Upon completion of the free radical polymerization of the monomer the energy source is discontinued to permit the free radically polymerized segments to recombine with the terminator portion of the iniferter to form polymer segments. The second monomer charge, if desired, is then introduced, and the new mixture is exposed to the energy source to cause dissociation of the terminator radical and free radical polymerization of the second monomer charge onto the first polymer segment, which now becomes the initiator of the second free radical polymerization. Upon completion of polymerization of the second monomer charge, the energy source is terminated and the terminator portion of the iniferter recombines with the reinforcing thermoplastic polymer block to provide a block copolymer.

-12-

The particular energy source and its intensity are selected to result in dissociation of the iniferter to free radicals. When employing a photoiniferter which will dissociate upon exposure to ultraviolet light radiation, an ultraviolet light source is utilized. The intensity and rate of radiation are
5 chosen to advance the polymerization at a reasonable rate without deleteriously affecting the polymer segment being produced. An ultraviolet light source having a wave length on the order of about 300 to about 400 nm spaced approximately 10 cm from the reactants to provide an exposure of 2 milliwatts per square centimeter has been found to produce suitable results. Reaction
10 times on the order of about 2 to about 50 hours have been found to be typical, depending upon the intensity of the radiation, with faster reaction times being observed at greater intensities.

The reactants and any solvent employed are charged into an energy source-transparent vessel and therein subjected to the energy source. If
15 the energy source is ultraviolet light radiation, a suitable ultraviolet light-transparent vessel is utilized. The reaction is preferably conducted in a vessel with agitation to permit uniform exposure of the reactants to the energy source. While most of the reactions have been conducted by employing a batch process, it is possible to utilize the same technology in a continuous polymerization
20 operation.

The reaction mixture may include a suitable inert solvent but it is not necessary since some of the monomeric materials are liquid themselves and may thus be charged into the reaction vessel without utilization of a solvent. The solvent, if utilized in the free radical polymerization, may be any substance
25 which is liquid in a temperature range of about -10°C to about 50°C, is substantially transparent to the energy source employed to permit dissociation of the iniferter to form free radicals, is essentially inert to the reactants and products, and will not otherwise adversely affect the reaction. Suitable solvents include but are not limited to those selected from the group consisting of water,
30 alkyl acetates such as ethyl acetate, alkanes such as hexane or heptane, alcohols such as methyl alcohol, ethanol, isopropyl alcohol, and mixtures thereof. The amount of solvent is generally about 30 to about 80 percent by weight based on the total weight of the reactants and solvent. In addition to solution polymerization herein described, the copolymerization may be carried out by
35 other well known techniques such as suspension, emulsion, and bulk polymerization.

It should be understood that minor amounts of the monomer forming the B block, the monomer forming the A block, if used, or both may be present as a homopolymer in the composition of the invention. Such minor amounts of homopolymer may be produced in an unwanted side reaction during polymerization of the photoiniferter polymer. Such amounts will typically be less than 10 parts of all homopolymer based upon 100 parts of the photoiniferter polymer.

II. Free-Radically (Co)Polymerizable Monomer(s)

The pressure sensitive adhesives, vibration damping materials, and structural materials of the present invention arise from the photopolymerization of a mixture of a photoiniferter polymer, compatible free-radically (co)polymerizable monomer(s), radiation-activatable crosslinking agent, and photoinitiator.

The compatible free-radically (co)polymerizable monomers are preferably identical to the monomers which comprise polymer segment B of the $I(BT)_n$ and/or $I(BAT)_n$ photoiniferter polymer. For example, if the B block of the photoiniferter polymer consists entirely of 2-ethylhexyl acrylate homopolymer, the photoiniferter polymer is preferably dissolved at the desired concentration in 2-ethylhexyl acrylate monomer (e.g., the free-radically (co)polymerizable monomer), which is then photopolymerized via the included photoinitiator. Similarly, if the B block of the photoiniferter polymer is a random copolymer of 2-ethylhexyl acrylate and N-vinylpyrrolidone, the free-radically (co)polymerizable monomer in which it is dissolved for further polymerization is preferably a mixture of N-vinylpyrrolidone and 2-ethylhexyl acrylate, in preferably approximately the ratios represented in the photoiniferter random copolymer, most preferably the exact same ratios. The photoiniferter polymer can be dissolved in the free-radically (co)polymerizable monomer by at least two different methods. The first method, which is preferred, involves forming the photoiniferter polymer by adding an iniferter to free-radically (co)polymerizable monomer(s) and not polymerizing to completion. This can also be accomplished by a second method which involves adding an iniferter to free-radically (co)polymerizable monomer(s), polymerizing to completion, removing the photoiniferter polymer, and dissolving or dispersing the photoiniferter polymer in additional free-radically (co)polymerizable monomer(s) which may or may not be the same monomers in the same ratios as those comprising polymer block B, preferably, however, the same.

III. Photoinitiators

The mixture of the free-radically (co)polymerizable monomer(s), radiation activatable crosslinking agent, and the photoiniferter polymer also contains a photoinitiator to induce polymerization of the free-radically (co)polymerizable monomers. Examples of photoinitiators which are useful include but are not limited to those selected from the group consisting of the benzoin ethers such as benzoin methyl ether, benzoin isopropyl ether, benzoin methyl ether, benzoin n-butyl ether, and methyl-o-benzoylbenzoates; substituted benzoin ethers such as anisole methyl ether; substituted acetophenones such as 2,2'-diethoxyacetophenone, 2,2 diethoxymethyl acetophenone, 1-phenyl-2-hydroxy-2 methyl-propane-1-one, hydroxy-cyclohexyl-phenyl-ketone, and 2,2'-dimethoxy-2-phenylacetophenone; substituted alpha-ketols such as 2-methyl-2-hydroxypropiophenone; aromatic sulfonyl chlorides such as 2-naphthalene sulfonyl chloride; photoactive oximes such as 1-phenyl-1,1-propanedione-2-(o-ethoxycarbonyl)-oxime; and mixtures thereof. The preferred photoinitiators are the substituted acetophenones. The photoinitiator is present in an amount of about 0.01 to about 5 parts by weight, preferably about 0.01 to about 0.5 parts by weight, based on the total weight of the free-radically (co)polymerizable monomer(s).

IV. Crosslinking Agents

The mixture of the photoiniferter polymer, free-radically (co)polymerizable monomers, and photoinitiator must also contain a radiation activatable crosslinking agent (i.e. a photocrosslinking agent). Preferred radiation activatable crosslinking agents include but are not limited to those selected from the group consisting of multifunctional acrylates such as 1,6-hexanediol diacrylate, 1,4-butanediol di(meth)acrylate, hexamethylenediol di(meth)acrylate, as well as those disclosed in U.S. Patent No. 4,379,201 (Heilmann et al.), such as trimethylolpropane triacrylate, pentaerythritol tetracrylate, ethylenediol di(meth)acrylate, and 1,12-dodecanediol diacrylate. Preferred multifunctional acrylates are those selected from the group consisting of 1,6-hexanediol diacrylate, 1,2-ethylene glycol diacrylate, 1,4-butanediol (meth)acrylate, and mixtures thereof. Other useful crosslinking agents include but are not limited to those selected from the group consisting of the chromophore-substituted triazines, such as those disclosed in U.S. Patent Nos. 4,329,384 and 4,330,590 (Vesley), e.g., 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine, 2,4-bis(trichloromethyl)-6-(3-methoxyphenyl)-s-

triazine, 2,4-bis(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine, 2,4-bis(trichloromethyl)-6-(3,4,5-trimethoxyphenyl)-s-triazine, 2,4-bis(trichloromethyl)-6-(3,4-methylenedioxyphenyl)-s-triazine, and 2,4-bis(trichloromethyl)-6-(4-methoxynaphthyl)-s-triazine, and in U.S. Patent
5 No. 4,181,752 (Martens), e.g., 2,4-bis(trichloromethyl)-6-(4-methoxystyryl)-s-triazine. The preferred triazine is 2,4-bis(trichloromethyl)-6-p-methoxystyrene-5-triazine. The crosslinking agent is present in an amount of from about 0.01 to about 5 parts, preferably about 0.05 to about 2 parts by weight, and most preferably about 0.1 to about 0.5 parts by weight, based upon the
10 total weight of the free-radically (co)polymerizable monomer(s) plus photoiniferter polymer.

V. Optional Additives

Other useful materials which can be blended into any of the
15 compositions of this invention include, but are not limited to, those additives selected from the group consisting of fillers, pigments, plasticizers, tackifiers, chain transfer agents, fibrous reinforcing agents, woven and nonwoven fabrics, foaming agents, antioxidants, stabilizers, fire retardants, viscosity adjusting agents, and mixtures thereof.

20 An especially useful filler material is hydrophobic silica as disclosed in U.S. Patent Nos. 4,710,536 and 4,749,590, (Klingen, et al.). In one preferred embodiment of the present invention, the pressure-sensitive adhesive layer further comprises from about 2 to about 15 parts by weight of a hydrophobic silica having a surface area of at least 10 m²/g based upon the
25 weight of the composition. Preferably, the surface area of the hydrophobic silica is from 50 to 400 m²/g.

VI. Pressure-Sensitive Adhesive Compositions of the Invention

The photoiniferter polymer contained in the pressure-sensitive
30 adhesive composition of the present invention comprises photoiniferter polymer selected from the group consisting of a monofunctional homopolymer of the formula I(BT)_n wherein n = 1 and the monomer charge from which B is formed comprises one type of monomer, a random copolymer of the formula I(BT)_n wherein n = 1 and the monomer charge from which B is formed
35 comprises more than 1 type of monomer, and an AB-type block copolymer of

the formula $I(BAT)_n$ wherein $n = 1$ and wherein the monomer charge from which B is formed comprises one or more types of monomer and the monomer charge from which A is formed comprises one or more types of monomer.

5 $I(BT)_n$

In the case wherein the PSA composition comprises a homopolymer of the formula $I(BT)_n$ wherein $n = 1$, B preferably comprises nonpolar monomer.

10 In the case where the pressure-sensitive adhesive composition comprises a random copolymer of the formula $I(BT)_n$, the monomer mixture in which the photoiniferter polymer is dissolved preferably comprises about 80 to about 100 percent by weight nonpolar monomer and about 0 to about 20 percent by weight polar monomer, preferably about 85 to about 99 percent by weight nonpolar monomer and about 1 to about 15 percent by weight polar monomer, and most preferably about 90 to about 99 percent by weight polar monomer and about 1 to about 10 percent by weight polar monomer, based upon the total weight of nonpolar plus polar monomer.

Useful polar monomers which $I(BT)_n$ can comprise include but are not limited to those selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, acrylonitrile, methacrylonitrile, N-vinylpyrrolidone, poly(ethylene oxide) acrylate, and mixtures thereof. Preferred polar monomers include those selected from the group consisting of acrylic acid, methacrylic acid, acrylamide, N-vinylpyrrolidone, and mixtures thereof. Most preferred polar monomers include those selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof.

25 Typical number average molecular weights of the B block of the $I(BT)_n$ random copolymer or homopolymer range from about 15,000 to about 500,000; preferably about 25,000 to about 250,000; and most preferably about 50,000 to about 200,000. The glass transition temperature (T_g) of the B block of the random copolymer or homopolymer should be in the range of about 30 -70°C to about 0°C, preferably about -60°C to about -10°C, and most preferably about -50°C to about -20°C, for reasons of processability and in order to achieve the requisite fourfold balance of desired PSA properties. Any combination of monomers which achieves the above parameters of molecular weight and T_g will be useful.

I(BAT)_n

In the case where the pressure-sensitive adhesive composition comprises an AB-type block copolymer, the B-block is characterized essentially as above, except that the number average molecular weight ranges sought for the B-block typically range from about 15,000 to about 500,000; preferably about 25,000 to about 500,000; and most preferably about 35,000 to about 250,000. The higher ranges are employed when PSAs having higher shear values are required.

Thermoplastic A-block monomers useful for preparing AB type block copolymers include but are not limited to those selected from the group consisting of methyl methacrylate, acrylonitrile, isobornyl acrylate, N-vinylpyrrolidone, glycidyl methacrylate, isobornyl methacrylate, isobutyl methacrylate and poly(styryl)methacrylate, and mixtures thereof. Preferred A-block monomers include those selected from the group consisting of methyl methacrylate, isobornyl acrylate, isobornyl methacrylate, and mixtures thereof. The preferred A-block monomer comprises methyl methacrylate. The glass transition temperature of the A block of the copolymer should be in the range of about 30°C to about 160°C, preferably about 50°C to about 150°C, and most preferably about 70°C to about 120°C. Typical number average molecular weights of the A block range from about 5,000 to about 100,000; preferably about 5,000 to about 50,000; and most preferably about 8,000 to about 30,000. The A-block can comprise either a homopolymer or a random copolymer, as long as the resultant AB-type block copolymer exhibits molecular weight and T_g values within the ranges prescribed. Within the AB-diblock copolymer, the A-block typically comprises about 2 percent to about 30 percent of the copolymer, preferably about 5 percent to about 25 percent, and most preferably about 10 percent to about 20 percent by weight of the diblock copolymer. These parameters provide a suitable balance of processability, cost, and desired PSA properties.

Within the AB-type block copolymer the B-block typically comprises about 70 percent to about 98 percent, preferably about 75 percent to about 95 percent, and most preferably about 80 percent to about 90 percent by weight based upon the weight of the block copolymer.

As indicated previously the PSA composition comprises about 10 to about 100 parts by weight photoiniferter polymer, preferably about 15 to about 60 parts by weight, most preferably about 15 to about 50 parts by weight.

The adhesive composition prepared in accordance with the present invention is easily coated upon suitable flexible or inflexible backing materials by conventional coating techniques to produce adhesive coated sheet materials in accordance with the present invention. The flexible backing
5 material may be any material conventionally utilized as a tape backing or any other flexible material. Typical examples of flexible backing materials employed as conventional tape backings which may be useful for the adhesive compositions of the present invention include but are not limited to those selected from the group consisting of paper, plastic films such as
10 polypropylene, polyethylene, polyvinyl chloride, polyester (e.g., polyethylene terephthalate), cellulose acetate and ethyl cellulose, as well as woven and nonwoven materials made from material and synthetic fibers.

Preferred tapes are made by coating adhesive on a backing or a core layer. The core layer may consist of a material including but not limited
15 to those selected from the group consisting of acrylates, polyethylenes, polypropylenes, neoprenes, polyolefins, polyurethanes, silicones, etc.

In a highly preferred embodiment, the core layer comprises an ultraviolet-radiation polymerized acrylic copolymer which may incorporate similar or dissimilar acrylic monomers in like or unlike thicknesses, having
20 similar or different additives from those acrylic copolymers contained in the adhesive layer. The core layers preferably comprise about 90 parts, most preferably at least about 95 parts of an alkyl acrylate polymer, and correspondingly, up to about 10 parts, most preferably up to about 5 parts of a strongly polar copolymerizable monomer.

Such core layer may be a foam-like layer, e.g., a monomer blend comprising microspheres maybe used. The microspheres may be glass or polymeric. The microspheres should have an average diameter of about 10 to about 200 micrometers, and comprise from about 5 to about 65 volume percent
25 of the core layer. The thickness of foam-like layers in preferred tapes of the invention range from about 0.3 mm to about 4.0 mm in thickness.

Especially preferred microspheres are polymeric microspheres, such as those described in U.S. Patent Nos. 3,615,972; 4,075,238; and 4,287,308. The microspheres are available from the Pierce & Stevens Company under the trade name "Microlite" in unexpanded form and "Miralit"
35 in expanded form. Similar microspheres are available from Kema Nord Plastics under the trade name "Expancel" and from Matsumoto Yushi Seiyaku under the trade name "Micropearl". In expanded form, the microspheres have

a specific density of approximately 0.02 to 0.036 g/cc. It is possible to include the unexpanded microspheres in the core layer and subsequently heat them to cause expansion, but it is generally preferred to mix in the expanded microspheres. This process ensures that the hollow microspheres in the final
5 core layer are substantially surrounded by at least a thin layer of adhesive.

Preferred glass microspheres have average diameters of about 80 micrometers. When glass microspheres are used, the pressure-sensitive adhesive layer should be at least 3 times as thick as their diameter, preferably at least 7 times. The thickness of layers containing such glass microspheres
10 should be at least six times, preferably at least twenty times that of each microsphere-free layer.

VII. Vibration Damping Compositions of the Invention

Vibration damping compositions of the present invention contain
15 photoiniferter polymer similar to the random-copolymer PSAs described above for the pressure-sensitive adhesive composition (i.e. an I(BT)_n polymer wherein n=1 or 2 and the monomer charge from which B is formed comprises more than 1 kind of monomer).

Useful polar monomers which B can comprise for this application
20 include but are not limited to those selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, acrylonitrile, methacrylonitrile, N-vinylpyrrolidone, poly(ethylene oxide)acrylate, and mixtures thereof. Preferred polar monomers include those selected from the group consisting of acrylic acid, methacrylic acid, acrylamide,
25 N-vinylpyrrolidone, and mixtures thereof. Most preferred polar monomers include those selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof.

Useful nonpolar monomers which B can comprise for this application include but are not limited to those selected from the group
30 consisting of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, methyl acrylate, isooctyl acrylate, n-butyl acrylate, iso-butyl acrylate, and mixtures thereof. Preferred nonpolar monomers include those selected from the group consisting of methyl methacrylate, n-butyl acrylate, isooctyl acrylate, and mixtures thereof. Most preferred nonpolar monomers include those selected
35 from the group consisting of n-butyl acrylate, isooctyl acrylate, and mixtures thereof.

In order to assure the adequate tackiness required for vibration-damping, polar monomer, if used, preferably constitutes a smaller percentage of the $I(BT)_n$ random copolymer. Thus, the free-radically (co)polymerizable monomer which the B block comprises (and in which the photoiniferter polymer may be dissolved) preferably comprises about 80 to about 100 percent by weight nonpolar monomer and about 0 to about 20 percent by weight polar monomer, more preferably about 90 to about 100 percent by weight nonpolar monomer and about 0 to about 10 percent by weight polar monomer, and most preferably about 95 to about 100 percent by weight nonpolar monomer and about 0 to about 5 percent by weight polar monomer.

Glass transition temperature ranges of the B block of the $I(BT)_n$ random copolymer for this application range from about -70°C to about -15°C , preferably about -60°C to about -30°C , and most preferably about -50°C to about -30°C in order to obtain the best vibration damping properties. B blocks of the $I(BT)_n$ random copolymers have number average molecular weights in the range of about 20,000 to about 50,000; preferably about 20,000 to about 40,000; and most preferably about 25,000 to about 40,000 in order to obtain the best vibration damping properties.

The vibration damping composition comprises about 10 to about 100 parts by weight photoiniferter polymer, preferably about 10 to about 50 parts by weight, and most preferably about 20 to about 30 parts by weight. If the concentration of the free-radically (co)polymerizable monomer(s) is too high, the photo-curing rate becomes too fast. If the concentration of free-radically (co)polymerizable monomer is too low, the viscosity of the composition becomes too high and the composition cannot be coated.

The high temperature-resistant vibration damping material of the invention is useful for applications in the automotive and computer industries, and possesses a loss tangent, $\tan\delta$, above about 0.5, preferably above about 0.7, and a storage modulus above about 1×10^7 dynes/cm², preferably between about 1×10^7 and about 5×10^8 dynes/cm² or higher at temperatures above about 50°C , preferably above about 75°C , and most preferably in the range of about 100° to about 150°C . In addition, the vibration damping material of the invention is stable against change of these characteristics following exposure of the vibration damping material to air at about 100°C for at least 1000 hours.

VIII. Structural Adhesive Compositions of the Invention

Structural adhesive compositions of the present invention contain photoiniferter polymers which comprise ABA-type triblock copolymers, synthesized via photoiniferter technology as described above, in which an I(T)_n iniferter wherein n = 2 is used to form I(BAT)_n triblock copolymer. The preferred iniferter for synthesis of ABA-type triblock copolymers is p-xylylene bis(N,N-diethyldithiocarbamate) because of its enhanced reactivity. The elastomeric central B-block has been described above with reference to AB-type diblock polymers useful in the pressure-sensitive adhesive compositions of the invention.

Useful nonpolar B-block monomers for this application include but are not limited to those selected from the group consisting of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, methyl acrylate, n-butyl acrylate, isobutyl acrylate, isobutyl methacrylate, isooctyl acrylate, and mixtures thereof. Preferred nonpolar B block monomers include those selected from the group consisting of n-butyl acrylate, n-butyl methacrylate, isooctyl acrylate, and mixtures thereof. Most preferred nonpolar B block monomers include those selected from the group consisting of n-butyl acrylate, isooctyl acrylate, and mixtures thereof.

Useful polar B block monomers for this application include but are not limited to those selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamide, acrylonitrile, methacrylonitrile, N-vinylpyrrolidone, poly(ethylene oxide)acrylate, and mixtures thereof. Preferred polar B block monomers include those selected from the group consisting of acrylic acid, methacrylic acid, acrylamide, N-vinylpyrrolidone, and mixtures thereof. Most preferred polar B block monomers include those selected from the group consisting of acrylic acid, methacrylic acid, and mixtures thereof.

Typical number average molecular weights of the B block for this application range from about 15,000 to about 500,000; preferably about 25,000 to about 250,000; and most preferably about 50,000 to about 200,000.

Useful A block monomers for this application include but are not limited to those selected from the group consisting of methyl methacrylate, acrylonitrile, isobornyl acrylate, N-vinylpyrrolidone, glycidyl methacrylate, isobornyl methacrylate, isobutyl methacrylate and poly(styryl)methacrylate, and mixtures thereof. Preferred A-block monomers include those selected from the

group consisting of methyl methacrylate, isobornyl acrylate, isobornyl methacrylate, and mixtures thereof. The preferred A-block monomer comprises methyl methacrylate.

5 Typical number average molecular weights of the A block for this application range from about 5,000 to about 100,000; preferably about 5,000 to about 50,000; and most preferably about 8,000 to about 30,000.

10 In order to assure the strength required for structural materials, the polar monomer, if used, preferably constitutes a smaller percentage of the B block of the ABA copolymer. Thus, the free-radically (co)polymerizable monomer which the B block comprises (and in which the photoiniferter polymer may be dissolved) preferably comprises about 80 to about 100 percent by weight nonpolar monomer and about 0 to about 20 percent by weight polar monomer, more preferably about 90 to about 100 percent by weight nonpolar monomer and about 0 to about 10 percent by weight polar monomer, and most
15 preferably about 95 to about 100 percent by weight nonpolar monomer and about 0 to about 5 percent by weight polar monomer.

20 In these structural adhesives, the A blocks preferably comprise a relative proportion of about 3 to about 30 percent by weight, preferably about 4 to about 20 percent by weight, and most preferably about 4 to about 8 percent by weight, relative to the total weight of the ABA copolymer. The concentration of ABA copolymer relative to the free radically (co)polymerizable monomer in the composition prior to photopolymerization is the same as stated for AB-type diblock PSAs discussed above.

25 The B block of I(BAT)_n must have a T_g of about -70°C to about 0°C, preferably about -60°C to about -10°C, and most preferably about -50°C to about -20°C, in order to obtain the best properties for structural adhesive applications. The A block of I(BAT)_n must have a T_g of about 30°C to about 160°C, preferably about 50°C to about 150°C, and most preferably about 70°C to about 120°C, in order to obtain the best properties for structural adhesive
30 applications.

IX. Method of Preparing and Curing the Compositions of the Invention

35 The compositions of the present invention are preferably prepared by dissolving or dispersing the photoiniferter (co)polymer into the corresponding free-radically (co)polymerizable monomer or monomer mixture, then adding a photoinitiator, a crosslinking agent, and any additives.

The composition is coated onto a flexible carrier web and polymerized in an inert, i.e., oxygen free, atmosphere, e.g., a nitrogen atmosphere. A sufficiently inert atmosphere can be achieved by covering a layer of the photoactive coating with a plastic film which is substantially transparent to ultraviolet radiation, and irradiating through that film in air using fluorescent-type ultraviolet lamps. If, instead of covering the polymerizable coating, the photopolymerization is to be carried out in an inert atmosphere, the permissible oxygen content of the inert atmosphere can be increased by mixing into the polymerizable monomer an oxidizable tin compound as taught in U.S. Patent No. 4,303,485 (Levens), which also teaches that such procedures will allow thick coatings to be polymerized in air. Useful oxidizable tin salts which are preferred because they readily dissolve in the above-described monomer or monomer mixture at room temperature include but are not limited to those chosen from the group consisting of stannous octoate, stannous chloride, stannous oleate, stannous naphthenate, stannous trifluoromethane sulfonate and tributyltin hydride. When an oxidizable tin salt is used, stannous octoate is preferred.

The present invention provides a crosslinked network of polymers via polymerization of one or more monomers in which the photoiniferter polymer is dissolved or dispersed.

In general, the blending of two or more structurally dissimilar polymers provides a convenient route for the modification of polymer properties to meet specific needs. Such polymer blends may exhibit increased flexibility, tensile strength, chemical resistance, ease of processing, and/or other improved physical and/or chemical properties.

However, most polymers are physically incompatible, due to the size of polymer chains, so that blends are formed only with some difficulty. In most cases, each polymer exists in its own phase and separation of the phases is readily observed. In extreme cases, phase separation is severe enough to negatively influence the physical properties of the resultant blend. When phase separation occurs on a microscale, however, positive effects, as noted above, result.

In the present invention, the process of polymerizing free-radically (co)polymerizable monomer in which a polymer (i.e., the photoiniferter polymer) has been dissolved or dispersed minimizes the possibility of large-scale phase separation. As monomer chains are formed from the free-radically (co)polymerizable monomer, existing chains of the

photoiniferter polymer are also randomly incorporated, due to the reactive end groups of the photoiniferter polymer. The resultant polymer has properties of a polymer network and a polymer blend. In addition, the two polymers of the final polymer network are very compatible, since their monomeric make-up may be identical (in the case of an I(BT)_n polymer dissolved in monomer from which B is formed) or may be partially identical (in the case of an I(BAT)_n polymer dissolved in monomer from which B is formed). That is, some or all of the monomers which comprise the photoiniferter polymer may be the same monomers in which that polymer is dissolved for further radiation curing, and preferably are the same monomers which the B block comprises.

Testing Procedures

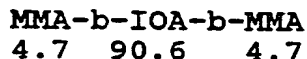
The following tests have been used to evaluate the adhesives of the invention.

Definitions of Terms

The number-average molecular weight (\bar{M}_n), and weight-average molecular weight (\bar{M}_w), are well known mathematical descriptions of the molecular weight distribution of a polymer sample.

Each of the foregoing is well known term used by polymer chemists and others. Further explanation of the derivation of these terms may be found in Experimental Methods in Polymer Chemistry, Wiley and Sons, 1981, Chapter 3 entitled "Molecular Weight Averages", pages 57-61.

The block photoiniferter copolymers which may be used in the present invention are described in a short-hand way depending upon the monomer forming each block. For example, MMA-b-IOA-b-MMA refers to a photoiniferter copolymer having blocks ("b") of polymerized methyl methacrylate ("MMA") and a block of polymerized isooctyl acrylate ("IOA"). Numbers appearing beneath each block refer to the portion of the weight percent of the total copolymer weight represented by the particular block. For example



refers to an ABA block copolymer having two A (polymethyl methacrylate) blocks of 4.7 weight percent each and a single B midblock (polyisooctyl acrylate) of 90.6 weight percent.

The following abbreviations and tradenames are used herein.

Abbreviations and Tradenames

	IOA	isooctyl acrylate
5	AA	acrylic acid
	MMA	methyl methacrylate
	S.S.	stainless steel
	min	minutes
	hr	hours
10	Temp.	temperature
	con.	concentration
	phr	parts per hundred
	BDC	benzyl N,N-diethyldithiocarbamate
	XDC	p-xylylene bis(N,N-diethyldithiocarbamate)
15	EA	ethyl acrylate
	HDDA	1,6-hexanediol diacrylate
	GMA	glycidyl methacrylate
	IBA	isobornyl acrylate
	NVP	n-vinylpyrrolidone
20	I.V.	inherent viscosity
	T _g	glass transition temperature
	PSA	pressure sensitive adhesive
	GPC	gel permeation chromatography
25	Irgacure™ 651	2,2-dimethoxy-2-phenyl acetophenone, from Ciba-Geigy
	Tan δ	loss tangent
	E'	storage modulus

Test Methods

30 The test methods used to evaluate the adhesives of the examples are industry standard tests. The test methods which characterize the polymers of this invention are those which demonstrate its molecular architecture. For this purpose gel permeation chromatography (GPC) and inherent viscosity measurement results have been obtained. The performance of the acrylic

35 polymers of the invention as PSA compositions has been measured in tape form with the adhesives coated by standard methods onto conventional film backings. The standard tests are described in detail in various publications of the

American Society for Testing and Materials (ASTM), Philadelphia, PA, and the Pressure Sensitive Tape Council (PSTC), Glenview, IL. The standard test methods are described in detail below. The reference source of each of the standard test methods is also given.

5

Gel Permeation Chromatography

The characterization of the molecular weight distribution of the polymers was by conventional gel permeation chromatography (GPC).

10 A Hewlett-Packard Model 1084B, high performance liquid chromatograph equipped with Styragel™ columns was used. The system was calibrated using polystyrene standards. All molecular weight averages are polystyrene equivalent molecular weights. The molecular weight averages and polydispersities are calculated according to accepted practices. GPC test methods are further explained in "Modern Size Exclusion Liquid
15 Chromatography" Practice of Gel Permeation Chromatography, John Wiley and Sons, 1979.

Shear Strength

(Reference: ASTM: D3654-78; PSTC-7)

20 The shear strength is a measure of cohesiveness or internal strength of an adhesive. It is based upon the amount of force required to pull an adhesive strip from a standard flat surface in a direction parallel to the surface to which it has been affixed with a definite pressure. It is measured in terms of time (in minutes) required to pull a standard area of adhesive coated
25 sheet material from a stainless steel test panel under stress of a constant, standard load.

The tests were conducted on adhesive coated strips applied to a stainless steel panel such that a 12.5 mm by 12.5 mm portion of each strip was in firm contact with the panel with one end portion of the tape being free. The
30 panel with coated strip attached was held in a rack such that the panel forms an angle of 178° with the extended tape free end which is then tensioned by application of a force of one kilogram applied as a hanging weight from the free end of the coated strip. The 178° angle (2° less than 180°) is used to negate any peel forces thus insuring that only the shear forces are measured in
35 an attempt to more accurately determine the holding power of the tape being tested. The time elapsed for each tape example to separate from the test panel is recorded as the shear strength.

90° Peel Adhesion

(Reference: ASTM D3330-78 PSTC-1 (11/75))

A strip of anodized aluminum 19 mm x 200 mm x 0.125 mm was positioned on one adhesive face of the tape sample. Pressure was applied to the aluminum by rolling with a 2 kg roller. The opposite face of the sample was then firmly bonded to a rigid substrate. After the specified dwell time, the sample was removed by pulling the aluminum strip at 90° to the adhesive surface at a speed of 30.5 cm/minute, noting the average adhesion in N/dm width, and the failure mode. Foam split (FS) is the most desired failure mode as it would indicate that adhesion to the substrate is stronger than the internal strength of the core layer.

Peel adhesion is the force required to remove a coated flexible sheet material from a test panel measured at a specific angle and rate of removal. In the examples, this force is expressed in Newtons per 100 mm (N/100 mm) width of coated sheet. The procedure followed is:

1. A 12.5 mm width of the coated sheet is applied to the horizontal surface of a clean glass test plate with at least 12.7 lineal cm in firm contact. A hard rubber roller is used to apply the strip.
2. The free end of the coated strip is doubled back nearly touching itself so the angle of removal will be 90°. The free end is attached to the adhesion tester scale.
3. The glass test plate is clamped in the jaws of a tensile testing machine which is capable of moving the plate away from the scale at a constant rate of 2.3 meters per minute.
4. The scale reading in Newtons is recorded as the tape is peeled from the glass surface. The data is reported as the range of numbers observed during the test.

Preparation of Samples for Shear

Strength and Peel Adhesion Testing

The shear holding power and peel adhesion are relative values which are influenced by how the samples to be tested are prepared and how they are coated. All of the examples reported in Tables I and II below were prepared by coating the composition to a dried thickness of 25 micrometers onto a primed 37 micrometer thick polyester film. The tapes were conditioned for 12 hours in a constant temperature testing room at 22°C and 50% relative humidity.

Tensile/Elongation

(Reference: ASTM D-638-89, PSTC 31)

This test method describes the determination of tensile and elongation of a sample, using an Instron Tensile Tests, Model 1122. An Instron Tester, "English" scale, equipped with clamp-type jaws and an "English" scale load cell was used. The jaw faces were coated with rubber or some other type of non-slip surface. The strip of material to be tested was 1 mm thick and approximately 10.2 cm longer than the initial jaw separation and 2.5 cm or less in width. Where applicable, the test material was cut in the machine direction. The equipment was set up as follows:

Expected Elongation	Cross-head Speed	Chart Speed	Gauge Length
Less than 100%	25.4 mm/min.	25.4 cm	(12.7 cm)
100% to 400%	25.4 mm/min.	25.4 cm	(5.1 cm)
More than 400%	50.8 mm/min.	25.4 cm	(2.5 cm)

The load range was selected so that the point of maximum force will range from between 30 to 90 percent of full scale. To begin the test, the test sample was aligned and clamped into the upper and lower jaws. The pen and chart were started in motion, and the tensile tester was started.

The stress plot was followed on the recording chart. If the chart limit was being approached, successively higher loads would be read. The test was allowed to continue until rupture of the sample.

Tensile strength is the maximum force applied to the test sample to obtain the tensile value. This was determined by counting the number of small divisions reached by the pen in its maximum travel to the right across the chart during the test. The maximum tensile value point and the point of rupture may or may not coincide. Maximum force was calculated in pounds by use of the following equation:

$$\text{Maximum Force} = \frac{\text{Load Range} \times \text{Maximum Small Divisions}}{100}$$

-29-

Tensile in pounds per width was reported and converted to KPa units.

Elongation is the maximum percent of stretch reached by the test specimen. To obtain the percent of elongation, the number of horizontal small divisions reached in the vertical chart dimension from the start to the point of specimen rupture was counted. This number is used to calculate the percent elongation by use of the following equation:

$$\% \text{ Elongation} = \frac{10 \times \text{Small Divisions} \times \text{Cross-head Speed}}{\text{Gauge Length} \times \text{Chart Speed}}$$

Loss Tangent/Storage Modulus

Procedures for determining the loss tangent and storage modulus of materials are well known in polymer physics and are described, for example, by Miles, *J. Appl. Phys.*, 33(4), 1422-1428 (1962). Loss tangent and storage modulus measurements reported herein were made using a Dynamic Shear Rheometer, Model CSR-1, from Melabs of Palo Alto, CA, that had been modified to ensure parallel alignment of the driver and pickup piezoelectric transducers. Stress on the sample and phase shift were read directly using state-of-the-art amplifiers and a phase network analyzer to monitor the output electrical signal.

Samples for testing were prepared by coating a 10 mm thick layer between release liners, then curing via UV radiation. The cured polymer was cut into 25 cm circles, the liner was removed, and a laminate of 10 circular samples, equal to 100 mm, was placed in the rheometer for testing.

For most applications, a layer of viscoelastic composition having a thickness of at least about 0.01 mm up to about 100 mm, preferably about 0.025 to about 100 mm, and most preferably about 0.05 to about 100 mm, is coated onto a suitable substrate by any of the techniques known in the art such as by spray, dip, or knife coating.

Examples

The following detailed description includes exemplary preparations of compositions in accordance with the invention. All parts, ratios, percentages, etc. in the examples and the rest of the specification are by weight unless otherwise specified.

Example 1 - Preparation of IOA/AA Monofunctional Random Copolymer and Pressure Sensitive Adhesives Prepared Therefrom

BDC was dissolved in an IOA/AA mixture in a pyrex bottle (see Table I for concentrations). The bottle was thoroughly purged with nitrogen, then sealed and irradiated with a bank of six General Electric 15-watt cylindrical black light bulbs while on a roller mill. Irradiation continued until the reaction mixture reached a viscosity sufficient for coating (i.e., about 20-30% conversion for this example although 5-30% conversion would be useful). Adhesive compositions were prepared from various amounts of photoiniferter polymer composition, crosslinker (HDDA), and 0.14% of photoinitiator 2,2-dimethoxy-2-phenyl acetophenone, which is available from Ciba Geigy under the tradename Irgacure™ 651. The mixture was agitated until the components were thoroughly mixed and then degassed in a vacuum desiccator. Adhesive films were prepared by knife coating the syrup onto the release coated surface of a 50 micrometer biaxially oriented poly(ethyleneterephthalate) (PET) film to provide a coating thickness of about 125 micrometers. The coated surface was then covered with a 50 micrometer release coated PET film. The "sandwich construction" emerging from the knife coater was cured by exposure to 580 to 600 mJ/cm² of UV radiation from a bank of fluorescent lamps. The film was cooled by blowing air against the bottom layer during irradiation to keep the temperature of the film below 85°C to avoid wrinkling. Ninety percent of the UV radiation was between 300 nm and 400 nm with a maximum at 351 nm as measured by an EIT model UR365CH1 Radiometer that was spectrally responsive between 300 and 400 nm. Table I shows peel adhesion and shear properties thus obtained. As can be seen, increases in crosslinker concentration afforded increased crosslinking density, hence generally increased shear but decreased peel adhesion. The active dithiocarbamate end groups can participate in chain transfer or chain termination reactions, and thus are chemically linked into the growing network. Further, the short-chain BDC-terminated random copolymers are incorporated into the growing IOA/AA chains from the 2,2-dimethoxy-2-phenyl acetophenone initiated photopolymerization, creating a comb-like polymer morphology which contributes to improved PSA properties. In general, the adhesives exhibited increased peel and shear adhesion with increasing BDC concentration. These observations are consistent with the fact that increasing BDC concentration affords an increased number of polymer

-31-

chains and generally shorter polymer chain lengths. However, when these properties are measured as a function of crosslinker concentration, a definite plateau is seen since excess crosslinking decreases desirable PSA properties.

TABLE I
PSA PROPERTIES OF DITHIOCARBAMATE CONTAINING IOA/AA POLYMERS
AT VARIOUS CONCENTRATIONS OF HDDA CROSSLINKER AND BDC

Polymer IOA/AA/BDC	HDDA (%)	90° Peel Adhesions (Newton/dm)				Shear(min.) 37.5 mm x 12.5 mm Room Temp.
		Glass		S.S.		
		20 min.	72 hr.	20 min.	54 hr.	
95/5/0 (con.)	0.2	68.2	48.4	33.0	35.2	10,000 +
95/5/0.19	0.2	90.2	55.0	37.0	44.0	485 pp
95/5/0.38	0.2	112.2	68.2	44.0	48.4	358 pp
95/5/0.75	0.2	110.0	112.2	46.2	50.6	221 pp
95/5/0 (con.)	0.4	57.2	44.0	30.8	30.8	347 pp
95/5/0.19	0.4	79.2	50.6	35.2	37.4	1,043 pp
95/5/0.38	0.4	88.6	47.2	37.4	44.0	245 pp
95/5/0.75	0.4	74.8	52.8	33.0	35.2	540 pp
95/5/0 (con.)	0.8	41.8	26.4	17.6	19.8	5,802 pp
95/5/0.19	0.8	63.8	46.2	26.4	30.8	351 pp
95/5/0.38	0.8	66.0	70.4	26.4	30.8	950 pp
95/5/0.75	0.8	58.0	39.6	26.4	30.8	910 pp
95/5/0 (con.)	1.2	30.8	22.0	13.2	17.6	299 pp
95/5/0.19	1.2	39.6	30.8	19.8	26.4	555 pp
95/5/0.38	1.2	50.6	37.4	22.0	28.6	220 pp
95/5/0.75	1.2	55.0	44.0	26.4	30.8	243 pp

pp = pop off panel (refers to failure between the adhesive and panel, the material still has good internal strength)
con. = control

Example 2 - Preparation of Isooctyl Acrylate/Acrylic Acid Monofunctional Random Copolymer and Vibration-Damping Compositions Prepared Therefrom

An isooctyl acrylate/acrylic acid random copolymer and vibration-damping compositions were made following the procedure of Example 1. The amount of BDC was varied as indicated in Table II. 0.2% amount of HDDA was used based upon the weight of the copolymer plus IOA/AA monomers. The cured compositions were tested for vibration damping characteristics as described above. Results are reported in Table II. Table II shows that cured compositions containing random IOA/AA copolymers made with increasing amounts of BDC exhibited improved vibration damping. Increasing the BDC concentration caused decreased polymer chain length which increased the tackiness and the overall vibration-damping properties. Table II shows that the cured composition with the highest concentration of BDC maintained excellent tan-delta and storage modulus values across a wide temperature range.

Example 3 - Preparation of a MMA-b-IOA Diblock Copolymer Acrylate and Pressure Sensitive Adhesives Prepared Therefrom

A. Preparation of a MMA-b-IOA Copolymer:

A solution of BDC in methyl methacrylate (MMA) was charged into a reaction bottle. The bottle was purged with nitrogen, sealed, then placed on a roller mill and irradiated with a bank of six GE 15 watt cylindrical black light bulbs. All of the MMA was allowed to polymerize in bulk. The resulting solid polymer was dissolved in ethyl acetate and IOA to yield a solution of 60% solids. The bottle was again purged with nitrogen, sealed, and irradiated. When the reaction was complete, ethyl acetate was removed to yield an MMA-b-IOA block copolymer having a reactive dithiocarbamate group at the end of the IOA block. For purposes of this example, 50 g of MMA and 100 g of IOA were used, yielding a copolymer that was 67 weight percent IOA and 33 weight percent MMA.

B. Preparation of a Pressure-Sensitive Adhesive:

The above MMA-b-IOA copolymer was dissolved in a mixture of IOA and AA following which photocrosslinker and photoinitiator were added to prepare a coatable syrup. The ratio of IOA to AA to diblock copolymer and the photocrosslinker (HDDA) concentration are shown in Table III. The Irgacure™ 651 photoinitiator (2,2-dimethoxy-2-phenyl acetophenone) was added at 0.14 percent by weight based on the total weight of the MMA-b-

-34-

IOA copolymer plus IOA and AA monomers. The syrup was coated at 5 mil thickness between liners, then cured by exposure to UV radiation (400 mJ/cm²). Table III shows the shear and peel adhesion values obtained for the adhesive. Again, the effect of higher crosslink density (increasing concentration of

5 HDDA) was demonstrated. Peel adhesions decreased while shear values increased.

TABLE II
VIBRATION-DAMPING PROPERTIES OF VIBRATION-DAMPING MATERIALS CONTAINING
RANDOM 95/5 IOA/AA COPOLYMERS AND VARYING AMOUNTS OF BDC

Temp. (°C)	Comparative Example 2a		Example 2b		Example 2c	
	Tan δ	E'	Tan δ	E'	Tan δ	E'
-50	0.1	3 X 10 ⁹	0.1	5 X 10 ⁹	0.1	5 X 10 ⁹
-25	0.8	1 X 10 ⁸	0.4	2 X 10 ⁸	0.4	2 X 10 ⁸
0	0.8	3 X 10 ⁶	0.8	2 X 10 ⁷	0.8	3 X 10 ⁷
25	0.5	1 X 10 ⁶	0.6	1 X 10 ⁶	0.8	6 X 10 ⁶
50	0.2	8 X 10 ⁵	0.6	8 X 10 ⁵	0.8	2 X 10 ⁶
100	0.15	5 X 10 ⁵	0.8	5 X 10 ⁵	0.7	1 X 10 ⁶

Comparative Example 2a: No BDC
 Example 2b: 0.19% BDC
 Example 2c: 0.75% BDC

TABLE III

**ADHESIVE PROPERTIES OF DIBLOCK CONTAINING
PSA COMPOSITIONS CURED IN PRESENCE OF DIFFERENT CONCENTRATIONS OF HDDA**

Polymer IOA/AA/MMA-b-IOA*	HDDA (%)	90° Peel Adhesions (Newton/dm)				Shear (min) 1.5 x 0.5 Room Temp.
		Glass		S.S.		
		20 min	72 hr	20 min	72 hr	
95/5/0 (con.)	0.1	90.2	90.2	72.6	81.4	10,000 +
95/5/0 (con.)	0.15	92.4	110.0	59.4	83.6	2,704 pp
95/5/0 (con.)	0.2	68.2	48.4	33.0	83.6	1,462 pp
95/5/0 (con.)	0.4	59.4	44.0	33.0	35.2	1,023 pp
95/5/10	0.1	195.8	206.8	129.8	127.6	6,000 pp
95/5/10	0.15	143.0	167.2	96.8	118.8	7,045 pp
95/5/10	0.2	121.0	140.8	116.6	112.2	5,650 pp
95/5/10	0.4	72.6	63.8	61.6	66.0	7,292 pp
95/5/15	0.1	33.0	44.0	33.0	59.4	1,840 pp
95/5/15	0.15	22.0	41.8	26.4	44.0	9,000 pp
95/5/15	0.2	22.0	24.2	22.0	41.8	5,239 pp
95/5/15	0.4	13.2	19.8	43.2	24.2	8,069 pp

pp = pop off panel
con. = control

* = MMA-b-IOA is a photoiniferter polymer

Example 4 - Preparation of MMA-b-(IOA/AA)-b-MMA Triblock Copolymer and Structural Pressure Sensitive Adhesives Prepared Therefrom

A. Preparation of an MMA-b-(IOA/AA)-b-MMA Triblock Copolymer:

5 A solution of IOA, AA and XDC in ethyl acetate was charged into a reaction bottle following which the bottle was purged with nitrogen. The bottle was sealed and placed on a roller mill and subjected to irradiation from six GE 15-watt cylindrical black light bulbs until conversion was complete, as monitored by NMR. To this reaction mixture was added
10 MMA, after which the bottle was again purged with nitrogen, sealed, and placed on the roller mill for further irradiation. The component amounts are set forth in Table IV. Conversion was again monitored by NMR. When the reaction was complete, the resulting triblock copolymer was used as indicated below.

15 B. Preparation of Structural Pressure Sensitive Adhesives:

The triblock copolymer of Example 4A was thoroughly mixed into a 9:1 ratio mixture of IOA and AA, along with Irgacure™ 651 2,2-dimethoxy-2-phenyl acetophenone photoinitiator, and HDDA
20 crosslinker. The component amounts are set forth in Table IV. The mixture was degassed in a vacuum desiccator, then knife-coated onto release-coated PET film, covered with a second release-coated PET film, and then cured by exposure to UV radiation. The cured polymer was removed from the liners. The adhesive properties of the cured polymer were evaluated and are reported
25 in Table IV.

TABLE IV

ADHESIVE PROPERTIES OF STRUCTURAL PSAS

Formulation ¹	90° Peel Adhesion (N/dm)				Shear ² min.	Tensile Strength kPa	Elongation %
	Glass		S.S.				
	20 min.	72 hr.	20 min.	72 hr.			
W	108	110	69	74	4500	1999	800
X	116	121	94	94	>5000	2344	750
Y	103	105	76	81	>5000	2654	950
Z	76	83	47	54	>5000	2034	650

¹All structural PSA composition formulations include 0.3% HDDA and 0.14% KB-1 photoinitiator, each based upon the total weight of triblock copolymer plus IOA/AA syrup. The PSA composition formulations each comprise a mixture of 10% by weight triblock copolymer and 90% by weight of an IOA/AA syrup that is 90% IOA and 10% AA. The triblock copolymer for each formulation was as follows:

- W. 8.3% MMA - b - 83.4% (IOA/AA 85/15) - b - 8.3% MMA
- X. 11.5% MMA - b - 77% (IOA/AA 85/15) - b - 11.5% MMA
- Y. 9.4% (GMA/MMA 12/88) - b - 71.2% (IOA/AA 85/15) - b - 9.4% (GMA/MMA 12/88)
- Z. 12.5% IBA - b - 75% (IOA/NVP 98/2) - b - 12.5% IBA

²Shear measurements are taken on 37.5 mm x 12.5 mm samples using a 1-Kg weight.

While this invention has been described in connection with specific embodiments, it should be understood that it is capable of further modification. The claims herein are intended to cover those variations which one skilled in the art would recognize as the chemical equivalent of what has
5 been described here.

CLAIMS

1. A radiation curable pressure sensitive adhesive composition comprising:

5 (a) 100 parts by weight of free radically (co)polymerizable monomer comprising:

(i) about 80 to about 100 parts by weight of (meth)acrylic acid ester(s) of monohydric alcohol(s), wherein said monohydric alcohol(s) comprise an average of about 1 to about 12 carbon atoms; and

10 (ii) about 0 to about 20 parts by weight of monoethylenically unsaturated polar monomer(s) which are copolymerizable with the (meth)acrylic acid ester(s);

(b) about 10 to about 100 parts by weight of a photoiniferter polymer selected from the group consisting of $I(BT)_n$ wherein n is an integer of 1 to 2, $I(BAT)_n$ wherein n is an integer of 1, and mixtures thereof, wherein

15 B comprises a polymer block having a T_g of between about -70°C and about 0°C wherein the polymer block B comprises polymerizable monoethylenically-unsaturated monomer(s);

A comprises a polymer block having a T_g of between 20 about $+30^\circ\text{C}$ and about $+160^\circ\text{C}$ wherein the polymer block A comprises polymerizable monoethylenically-unsaturated monomer(s);

I represents a free-radical initiator portion of an iniferter of the formula $I(T)_n$, wherein

25 T represents the terminator portion of said iniferter; and $I(T)_n$ is capable upon being subjected to an appropriate energy source of forming free radicals $I(\cdot)_n$ and $nT\cdot$ wherein $I\cdot$ is a highly reactive free radical capable of initiating free radical polymerization, and $T\cdot$ is a less reactive free radical which is generally much less capable of initiating free radical polymerization than $I\cdot$ but will rejoin with $I(\cdot)_n$ upon termination

30 of said energy source;

(c) about 0.1 to about 5 parts by weight of a radiation-activatable crosslinking agent based upon the total weight of (a) plus (b); and

35 (d) about 0.01 to about 5 parts by weight of a photoinitiator based upon the weight of (a).

2. A radiation curable vibration damping composition comprising:
- (a) 100 parts by weight of free-radically (co)polymerizable monomer comprising:
- 5 (i) about 80 to about 100 parts by weight of (meth)acrylic acid ester(s) of monohydric alcohol(s), wherein the monohydric alcohol(s) comprise an average of about 1 to about 12 carbon atoms;
- (ii) about 0 to about 20 parts by weight of monoethylenically unsaturated polar monomer(s) that are copolymerizable with the (meth)acrylic acid ester(s);
- 10 (b) about 10 to about 100 parts by weight of a photoiniferter polymer selected from the group consisting of $I(BT)_n$, and mixtures thereof, wherein
- n is an integer of 1 to 2;
- B comprises a polymer block having a T_g of between
- 15 about -70°C and about -15°C , and a number average molecular weight ranging from about 20,000 to about 50,000, wherein polymer block B comprises polymerizable monoethylenically-unsaturated monomer(s);
- I represents a free-radical initiator portion of an iniferter of the formula $I(T)_n$, wherein
- 20 T represents the terminator portion of the iniferter; and
- $I(T)_n$ is capable upon being subjected to an appropriate energy source of forming free radicals $I(\cdot)_n$ and $nT\cdot$ wherein $I\cdot$ is a highly reactive free radical capable of initiating free radical polymerization, and $T\cdot$ is a less reactive free radical which is generally much less capable of initiating
- 25 free radical polymerization than $I\cdot$ but will rejoin with $I(\cdot)_n$ upon termination of the energy source;
- (c) about 0.1 to about 5 parts by weight of a radiation-activatable crosslinking agent based upon the total weight of (a) plus (b); and
- 30 (d) about 0.01 to about 5 parts by weight of a photoinitiator based upon the weight of (a).

3. A radiation curable structural adhesive composition comprising:

(a) 100 parts by weight of free radically (co)polymerizable monomer comprising:

5 (i) about 80 to about 100 parts by weight of (meth)acrylic acid ester(s) of monohydric alcohol(s), wherein the monohydric alcohol(s) comprise an average of about 1 to about 12 carbon atoms; and

(ii) about 0 to about 20 parts by weight of monoethylenically unsaturated polar monomer(s) that are copolymerizable with the (meth)acrylic acid ester(s);

10 (b) about 10 to about 100 parts by weight of a photoiniferter polymer selected from the group consisting of $I(BAT)_n$, and mixtures thereof wherein

n is an integer of 2;

15 B comprises a polymer block having a T_g of between about 0°C and about -70°C , wherein polymer block B comprises polymerizable monoethylenically-unsaturated monomer(s);

A comprises a polymer block having a T_g of about 30°C to about 160°C wherein polymer block A comprises polymerizable monoethylenically-unsaturated monomer(s);

20 I represents a free-radical initiator portion of an iniferter of the formula $I(T)_n$, wherein

T represents the terminator portion of said iniferter; and

25 $I(T)_n$ is capable upon being subjected to an appropriate energy source of forming free radicals $I(\cdot)_n$ and $nT\cdot$ wherein $I\cdot$ is a highly reactive free radical capable of initiating free radical polymerization, and $T\cdot$ is a less reactive free radical which is generally much less capable of initiating free radical polymerization than $I\cdot$ but will rejoin with $I(\cdot)_n$ upon termination of said energy source;

30 (c) about 0.1 to about 5 parts by weight of a radiation-activatable crosslinking agent based upon the total weight of (a) plus (b); and

(d) about 0.01 to about 5 parts by weight of a photoinitiator based upon the weight of (a).

4. The composition of claim 2 wherein the said crosslinking agent is selected from the group consisting of multifunctional vinyl monomers such as ethylenediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, hexamethylenediol di(meth)acrylate, trimethylolpropane triacrylate, pentaerythritol tetracrylate, 1,12-dodecanediol diacrylate, 2,4-bis (trichloromethyl)-6-p-methoxystyrene-5-triazine, chromophore haolmethyl-5-triazines, and mixtures thereof.
5. A pressure sensitive adhesive comprising the cured composition of claim 1.
6. A vibration damping adhesive comprising the cured composition of claim 2.
7. A structural adhesive comprising the cured composition of claim 3.
8. A method of making a pressure-sensitive adhesive comprising the steps of:
- (a) providing a radiation curable pressure-sensitive adhesive composition according to claim 1; and
- (b) exposing said composition to electromagnetic radiation to polymerize said composition to a pressure-sensitive adhesive.
9. A method of making a vibration damping adhesive comprising the steps of:
- (a) providing a radiation curable vibration damping composition according to claim 2; and
- (b) exposing said composition to electromagnetic radiation to polymerize said composition to a vibration damping adhesive.
10. A method of making a structural adhesive comprising the steps of:
- (a) providing a radiation curable structural adhesive composition according to claim 3; and
- (b) exposing said composition to electromagnetic radiation to polymerize said composition to a structural adhesive.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02528

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09J4/06; C08F287/00

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C09J ; C08F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 449 619 (MINNESOTA MINING AND MANUFACTURING COMPANY) 2 October 1991 see the whole document ---	1,5,8
A	EP,A,0 434 334 (MINNESOTA MINING AND MANUFACTURING COMPANY) 26 June 1991 see claims 1-10 ---	1-10
A	EP,A,0 286 376 (MITSUBISHI PETROCHEMICAL) 12 October 1988 cited in the application ---	1-10
A	EP,A,0 349 270 (MINNESOTA MINING AND MANUFACTURING COMPANY) 3 January 1990 -----	1,3,5,7, 8,10

¹⁰ Special categories of cited documents :¹⁰¹⁰ "A" document defining the general state of the art which is not
considered to be of particular relevance¹⁰ "E" earlier document but published on or after the international
filing date¹⁰ "L" document which may throw doubts on priority claim(s) or
which is cited to establish the publication date of another
citation or other special reason (as specified)¹⁰ "O" document referring to an oral disclosure, use, exhibition or
other means¹⁰ "P" document published prior to the international filing date but
later than the priority date claimed¹⁰ "T" later document published after the international filing date
or priority date and not in conflict with the application but
cited to understand the principle or theory underlying the
invention¹⁰ "X" document of particular relevance; the claimed invention
cannot be considered novel or cannot be considered to
involve an inventive step¹⁰ "Y" document of particular relevance; the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such docu-
ments, such combination being obvious to a person skilled
in the art.¹⁰ "&" document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

10 JUNE 1993

Date of Mailing of this International Search Report

25. 06. 93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

ANDRIOLLO G.R.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9302528
SA 71712

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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10/06/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0449619	02-10-91	None	
EP-A-0434334	26-06-91	JP-A- 4235108	24-08-92
EP-A-0286376	12-10-88	JP-A- 1026619	27-01-89
EP-A-0349270	03-01-90	AU-B- 614140	22-08-91
		AU-A- 3523989	04-01-90
		JP-A- 2103277	16-04-90

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